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Zeneca Limited
15 Stanhope Gate
London
W1Y 6LN

Patents ADP number *(if you know it)* — 6254007002

If the applicant is a corporate body, give the country/state of its incorporation — United Kingdom

4. Title of the invention — Composition

5. Name of your agent *(if you have one)*

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MAYALL, John
Zeneca Specialties
Hexagon House
P O Box 42
Blackley
Manchester M9 8ZS

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APPLICANTS

Zeneca Limited

TITLE

COMPOSITION

COMPOSITION

This invention relates to inks containing certain polyurethanes and to their use in ink jet printing.

Ink jet printing methods involve a non-impact printing technique for printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle. The most popular ink jet printers are the thermal and piezoelectric ink jet printers.

EP 0769 509 describes a high molecular weight chain extended polyurethane formed from a coloured polyurethane prepolymer for use in ink jet printers with piezo heads. However this composition is not ideal for use in ink jet printers with thermal heads because the use of heat results in nozzle blockage and other operability problems.

There is a need for inks which are suitable for both thermal and piezo ink jet printers, have high colour strength and produce images having a high light-fastness and water-fastness when printed on a substrate.

According to a first aspect of the present invention there is provided an ink comprising a water-dissipatable polyurethane, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent.

The Polyurethane

The water-dissipatable polyurethane has preferably been obtained from the reaction of a mixture comprising the components:

i) at least one organic polyisocyanate; and

ii) at least one isocyanate-reactive compound providing dispersing groups.

The water-dissipatable polyurethane preferably has a weight average molecular weight (Mw) less than 25,000 because this can lead to an improved performance of inks containing the polyurethane, especially for use in thermal ink jet printers. The Mw of the polyurethane is preferably less than 20,000, more preferably from 1000 to 15,000, especially from 1000 to 8000, more especially from 1000 to 7000. Mw may be measured by gel permeation chromatography ("gpc").

The gpc method used for determining Mw preferably comprises applying the polyurethane to a chromatography column packed with cross-linked polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the Mw of the polyurethane compared to a number of a polystyrene standards of a known Mw. Suitable cross-linked polystyrene/divinyl benzene chromatography columns are commercially available from Polymer Laboratories.

If the gpc method for determining Mw does not work for any reason then other methods to determine Mw may be used, for example dynamic light scattering.

Component i) may be any organic polyisocyanate known in the art, preferably having two isocyanate groups, and may for example be an aliphatic, cycloaliphatic, aromatic or araliphatic isocyanate. Examples of suitable organic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyl-methane diisocyanate and its hydrogenated derivative, 2,4'-diphenylmethane diisocyanate and its hydrogenated derivative, and 1,5-naphthylene diisocyanate. Mixtures of the polyisocyanates can be used, particularly isomeric mixtures of the toluene diisocyanates or isomeric mixtures of the diphenylmethane diisocyanates (or their hydrogenated derivatives), and also organic polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred organic polyisocyanates include cycloaliphatic polyisocyanates, especially isophorone diisocyanate, and aliphatic isocyanates, especially 1,6-hexamethylene diisocyanate or hydrogenated 4,4-diphenyl methyl diisocyanate. A small quantity of triisocyanates may be included as part of component i) but this amount preferably does not exceed 5% by weight relative to the total weight of component i). In a preferred embodiment component i) consists of a mixture of diisocyanate and from 0 to 5% of triisocyanate by weight relative to the diisocyanate.

Component ii) preferably has at least one, and preferably has two, isocyanate-reactive groups. Preferred isocyanate-reactive groups are selected from -OH, $-NH_2$, -NH- and -SH. Isocyanate-reactive compounds having three isocyanate-reactive groups may be present, preferably in low levels not exceeding 5% by weight relative to the total weight of component ii). These isocyanate-reactive groups are capable of reacting with an isocyanate (-NCO) group in component i) or component iii).

The dispersing groups provide the facility of self-dispersibility and solubility to the polyurethane in ink media, especially in water. The dispersing groups may be ionic, non-ionic or a mixture of ionic and non-ionic dispersing groups. Preferred ionic dispersing groups include cationic quaternary ammonium groups, sulphonic acid groups and carboxylic acid groups.

The ionic dispersing groups may be incorporated into the polyurethane in the form of a low molecular weight polyol or polyamine bearing the appropriate ionic

dispersing groups. Preferred isocyanate-reactive compounds providing dispersing groups are diols having one or more carboxylic acid groups, more preferably dihydroxy alkanoic acids, especially 2,2-dimethylol propionic acid.

The carboxylic and sulphonic acid groups may be subsequently fully or partially neutralised with a base containing a cationic charge to give a salt. If the carboxylic or sulphonic acid groups are used in combination with a non-ionic dispersing group, neutralisation may not be required. The conversion of any free acid groups into the corresponding salt may be effected during the preparation of the polyurethane and/or during the preparation of an ink from the polyurethane.

Preferably the base used to neutralise any acid dispersing groups is ammonia, an amine or an inorganic base. Suitable amines are tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example $N^{+}(CH_3)_4OH^{-}$, can also be used. Generally a base is used which gives the required counter ion desired for the ink which is prepared from the polyurethane. For example, suitable counter ions include Li^{+}, Na^{+}, K^{+}, NH_4^{+} and substituted ammonium salts.

Non-ionic dispersing groups may be in-chain, pendant or terminal groups. Preferably non-ionic dispersing groups are pendant polyoxyalkylene groups, more preferably polyoxyethylene groups. The non-ionic groups may be introduced into the polyurethane in the form of a compound bearing non-ionic dispersing groups and at least two isocyanate-reactive groups or may be introduced as a capping reagents with only one isocyanate-reactive group on a compound bearing non-ionic dispersing groups.

The nature and level of dispersing groups in the polyurethane influences whether a solution, dispersion, emulsion or suspension is formed on dissipation of the polyurethane.

The dispersing group content of the polyurethane may vary within wide limits but is preferably sufficient to make the polyurethane form stable ink-jet printing inks in water and aqueous media. The polyurethane is preferably soluble in water, although minor amount of the polyurethane may be insoluble in water and exist as dissipated particles when mixed with aqueous media or water.

Preferably the proportion of insoluble, water-dissipatable polyurethane is less than 50%, preferably less than 40% and most preferably less than 30% by weight relative to the total weight of the polyurethane. The size of insoluble polyurethane particulates when dissipated in an ink is preferably less than 100nm, and more preferably less than 60nm.

Preferably the polyurethane is not isocyanate terminated.

Terminating compounds may be used to cap off any excess isocyanate or isocyanate reactive end groups in the polyurethane resulting from the reaction of components i) and ii). Compounds having one isocyanate-reactive group include for

example monoalcohols, monoamines and monothiols, especially isopropanol. The terminating compounds may also bear dispersing groups as hereinbefore described. If there any excess isocyanate-reactive end groups in the polyurethane resulting from the reaction of component ii), these may optionally be capped off by the addition of compounds having one isocyanate group, for example alkyl monoisocyanates.

The polyurethane may be prepared in a conventional manner by reacting the components having isocyanate groups with the components having isocyanate-reactive groups. Substantially anhydrous conditions are preferred. Temperatures of from 30°C and 130°C are preferred and the reaction is continued until the reaction between the isocyanate groups and the isocyanate-reactive groups is substantially complete.

The relative amounts of components i) and ii) are preferably selected such that the mole ratio of isocyanate groups to isocyanate-reactive groups is about 1:1. A two stage process may be utilised where a prepolymer is prepared either in solvent or as a melt, wherein the mole ratio of isocyanate groups to isocyanate-reactive groups from about 1.3:1 to 2:1, preferably from about 1.4:1 to 2:1, followed by reacting any excess isocyanate end groups with a terminating compound.

Alternatively a prepolymer may be prepared wherein the ratio of isocyanate groups to isocyanate-reactive groups from about 1:1 to 1:2, preferably from about 1:1 to 1:1.3. The excess isocyanate-reactive end groups may optionally be terminated with a terminating compound.

Preferably the polyurethane is not chain-extended. Preferably the reaction is performed entirely under anhydrous conditions, resulting in no substantial extension of polyurethane on mixing the polyurethane with water or water mixed with chain extenders.

If desired a catalyst may be used to assist polyurethane formation. Suitable catalysts include butyl tin dilaurate, stannous octoate and tertiary amines as known in the art .

The polyurethane of the present invention may be purified if desired in the usual way for colorants used in ink jet printing inks. For example a mixture of the polyurethane and water may be purified by ion-exchange, filtration, reverse osmosis, dialysis, ultra-filtration or a combination thereof. In this way one may remove co-solvents used for the polymerisation, low molecular weight salts, impurities and free monomers.

The Colorant

The colorant is preferably soluble in the polyurethane. Preferably the Colorant is soluble in organic solvents and insoluble in water, for example it is free from sulpho and carboxy groups. In a preferred embodiment the colorant is a dye, more preferably a dye which is soluble in organic solvents and insoluble in water, especially a disperse dye.

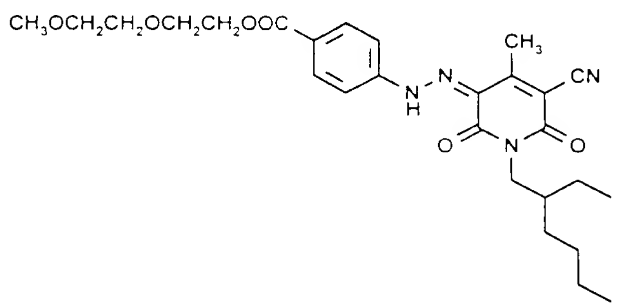
The colorant may be a single component colorant or multi-component colorant, for example it may be a mixture of different dyes. By using a mixture of different dyes as the colorant one may achieve greater flexibility in colour of the ink.

Useful classes of colorants include anthraquinones, phthalocyanines, pyrrolines, triphenodioxazines, methines, benzodifuranones, coumarins, indoanilines, benzenoids, xanthenes, phenazines, solvent soluble sulphur dyes, quinophthalones, pyridones, aminopyrazoles, pyrollidines, styrylics and azoics. Examples of preferred azoics are monoazo, disazo and trisazo disperse dyes each, of which are optionally metallised and solvent soluble dyes; especially preferred azoics contain heterocyclic groups. The Colour Index International lists suitable disperse and solvent soluble dyes, examples of which include Solvent Blue 63, Disperse Blue 24, Solvent Black 3, Solvent Black 35 and Disperse Red 60.

Further examples of disperse dyes are given in the Colour Index, 3rd Edition, Volume 2, pages 2483 to 2741 and further examples of solvent soluble dyes are given in Volume 3, pages 3566 to 3647 and each of these dyes is included herein by reference

Preferred colorants for use in the inks include:

$CuPc(SO_2NHCH_2CH_2CH_2N(CH_3)_{2.7}(SO_3H)_{0.3}$ in which Pc is phthalocyanine; and



Water-Miscible Organic solvents

Suitable water-miscible organic solvents include C_{1-5}-alkanols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol and isobutanol; amides, e.g. dimethylformamide and dimethylacetamide; ketones and ketone alcohols, e.g. acetone and diacetone alcohol; C_{2-4}-ether, e.g. tetrahydrofuran and dioxane; alkylene glycols or thioglycols containing a C_2-C_6 alkylene group, e.g. ethylene glycol, propylene glycol, butylene glycol, pentylene glycol and hexylene glycol; poly(alkylene-glycol)s and thioglycol)s, e.g. diethylene glycol, thiodiglycol, polyethylene glycol and polypropylene glycol; polyols, e.g. glycerol and 1,2,6-hexanetriol; and lower alkyl glycol and polyglycol ethers, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol; cyclic esters and cyclic amides, e.g. optionally substituted pyrrolidones; sulpholane; and mixtures containing two or more of the aforementioned water-miscible organic solvents.

Preferred water-miscible organic solvents are C_{1-6}-alkyl mono ethers of C_{2-6}-alkylene glycols and C_{1-6}-alkyl mono ethers of poly(C_{2-6}-alkylene glycols). Cyclic amides are especially preferred.

Water-immiscible Organic Solvents

Suitable water-immiscible organic solvents include aromatic hydrocarbons, e.g. toluene, xylene, naphthalene, tetrahydronaphthalene and methyl naphthalene; chlorinated aromatic hydrocarbons, e.g. chlorobenzene, fluorobenzene, chloronaphthalene and bromonaphthalene; esters, e.g. butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate; alcohols having six or more carbon atoms, e.g. hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol and phenoxy butanol; ethers having at least 5 carbon atoms, preferably C_{5-14} ethers, e.g. anisole and phenetole; nitrocellulose, cellulose ether, cellulose acetate; low odour petroleum distillates; turpentine; white spirits; naphtha; isopropylbiphenyl; terpene; vegetable oil; mineral oil; essential oil; and natural oil; C_8-C_{12} substituted pyrrolidones; and mixtures of any two or more thereof Benzyl alcohol is especially preferred.

Preferred Ink Formulations

The inks according to the first aspect of the invention may be prepared by mixing the polyurethane, colorant, water, water-miscible organic solvent and water-immiscible organic solvent in any order. Suitable mixing techniques are well known in the art, for example agitation, ultrasonication or stirring of the components. The polyurethane may be present in the ink in any form suitable for inkjet printing, for example the form of a dispersion, emulsification, suspension, solution or a combination thereof.

Preferably the ink is prepared by mixing a dissipation of the polyurethane in a first liquid medium with a solution of the colorant in a second liquid medium, wherein the first liquid medium comprises water and optionally a water-miscible organic solvent and the second liquid medium comprises a water-immiscible organic solvent and optionally a water-miscible organic solvent.

The weight ratio of water-miscible organic solvent to water-immiscible organic solvent in the ink is preferably 19:1 to 1:1, more preferably 8:1 to 1:1, especially 5:1 to 1:1.

The amount of colorant and water-dissipatable polyurethane contained in the ink will vary according to the depth of shade required. Typically, however, the ink will comprise:

(a) from 0.5 to 50 parts. more preferably 2 to 20 parts. especially 4 to 12 parts

of a water-dissipatable polyurethane (preferably having a weight average molecular weight less than 25,000);

(b) from 0.1 to 20 parts, more preferably 0.5 to 10 parts, especially 0.5 to 3 parts of colorant;

(c) from 40 to 90 parts, more preferably from 50 to 80 parts of water;

(d) from 2 to 30 parts, more preferably 5 to 15 parts, especially from 8 to 12 parts of a water-immiscible organic solvent; and

(e) from 2 to 60 parts, more preferably from 5 to 25 parts, especially from 10 to 20 parts of a water-miscible organic solvent;

wherein all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) + (e) add up to 100.

The number of parts of the water-dissipatable polyurethane is calculated on a 100% solids basis. For example 50g of a 20% solids polyurethane is taken as 10g of polyurethane.

The ink optionally contains a biocide, for example Proxel GXL (Proxel is a trade mark of Zeneca Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, for example Projet 900NP (Projet is a trade mark of Zeneca Limited), or a fluorescent brightener, for example C.I.Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the ink compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference.

The ink preferably has a pH from 3 to 11, more preferably from 4 to 10. The pH selected will depend to some extent on the desired cation for any acid groups present in the polyurethane and the materials used to construct the ink jet printer head. The desired a pH may be obtained by the addition of an acid, base or a pH buffer. Where a base is used this is preferably the same base as was used to neutralise the anionic dispersing group during the preparation of the polyurethane.

The viscosity of the ink is preferably less than 20cp, more preferably less than 15cp, especially less than 10cp, at 20°C.

The inks of the present invention have the advantage that they are suitable not only for the use in piezoelectric ink jet printers but also in thermal and continuous ink jet printers. Many other inks based on polymers work poorly or even not at all in thermal ink jet printers.

Inks of the invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the inks show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto an ink according to the first aspect of the present invention by means of an ink jet printer.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character.

According to a further feature of the invention there is provided an ink jet printer cartridge containing an ink as hereinbefore defined.

The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise. In the examples, compounds referred to by reference to CI numbers are the dyestuffs identified by these numbers in the Colour Index International, 3rd Edition, 3rd Revision.

Example 1

Stage 1 - Preparation of a Water Dissipatable Polyurethane ("Resin 1")

(100% chain terminated with MPEG750)

Components 1,2,3 and 5 were charged to a stirred reaction vessel under a nitrogen atmosphere, heated to 50°C and component 6 was added. The reaction exothermed by about 3°C and was then maintained at 90-95°C for 3 hours. A sample of the resultant mixture (3.519g) was removed to determine the %NCO content (found to be 4.71%). Component 4 followed by component 7 were added to the mixture and the temperature was maintained at 90°C until the isocyanate band as determined by an IR spectrum had almost disappeared (2 hours).

Component 8 was added to the stirred mixture at 50°C and allowed to mix for 10 minutes. The resultant mixture at 50°C was dispersed into component 9 at 30°C. During the addition, the temperature of the water rose to about 42°C. The mixture was stirred for a further one hour, cooled to room temperature, and filtered through a 50μm filter.

The resultant water-dissipated polyurethane in water was found to have a solids content of 24.4% and a pH of 7. The weight average molecular weight (MW) was determined by applying the polyurethane to a gpc column packed with cross-linked

polystyrene/divinyl benzene, eluting with tetrahydrofuran at 40°C and assessing the MW compared to a number of polystyrene standards of known MW. The Mw was found to be = 4791 (Mn was 1729).

Stage 2 - Preparation of Ink 1

A sample of a solvent soluble phthalocyanine dye (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of the water-dissipatable polyurethane resulting from Stage 1 (40.9g, 24.4 % w/w dissipation in water) and water (28.1g) were added and the mixture was shaken to give Ink 1 having the formulation:

Component	Amount (g)
Dye	1
Resin 1	40.9 (24.4% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrollidone (Miscible)	20
Water	28.1
	100

Example 2

Stage 1 - Preparation of a Water-dissipatable Polyurethane ("Resin 2")

(100% chain terminated with Jeffamine M1000 available from Huntsman Corporation, USA)

Component Number	Component Name	Weight(g)
1	Isophorone diisocyanate	492.21
2	polypropylene glycol of molecular weight 1000	357.8
3	dimethylol propionic acid	150
4	Jeffamine M1000	1543.35
5	N-methylpyrrolidone	250
6	dibutyl tin dilaurate	1.0
7	dimethyl ethanol amine	99.72
8	distilled water	7282.5

Components 1,2,3 and 5 were charged to a stirred reaction vessel under a nitrogen atmosphere, heated to 50°C and component 6 was added. The reaction exothermed by about 3°C and was then maintained at 90-95°C for 3 hours. A sample of the resultant mixture (3.519g) was removed to determine the %NCO content (found to be 4.71%). Component 4 was added to the mixture and the temperature maintained at

90°C for a further hour or until the isocyanate band as determined by an the IR spectrum had disappeared.

Component 7 was added to the stirred mixture at 50 °C and allowed to mix for 10 minutes. The resultant mixture at 50 °C was dispersed into component 8 at 30 °C. During the addition, the temperature of the water rose to about 42°C. The mixture was stirred for a further one hour, cooled to room temperature and filtered through a 50μm filter.

The resultant mixture of water and water-dissipatable polyurethane was found to have a solids content of 24.2% and a pH of 8.3. The Mw was determined by GPC to be 6597.

Stage 2 - Preparation of Ink 2

A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of the water-dissipatable polyurethane described in Example 2, Stage 1 (41.3g 24.19% w/w solution in water) and water (27.7g) were added and the mixture was shaken to give Ink 2 having the formulation:

Component	Amount (g)
Dye	1
Resin 2	41.3 (24.19% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrollidone (Miscible)	20
Water	27.7
	100

Comparative Example 1 - High Molecular Weight Polyurethane

Preparation of Ink 3

An ink was prepared using a high molecular weight commercially available polyurethane dispersion called Neorez R961 (Obtained from Zeneca Resins).

A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of Neorez R961 (26.5g, 34% w/w dispersion in water) and water (32.5g) was added and the mixture was shaken to give Ink 3 having the formulation:

Component	Amount (g)
Dye	1
Neorez R961	26.5 (34% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrollidone (Miscible)	20
Water	32.5
	100

Comparative Example 2 - No Polyurethane

A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. Water (69g) was added and the mixture was shaken to give a Ink 4 having the formulation:

Component	Amount (g)
Dye	1
Benzyl alcohol (Immiscible)	10
2-pyrrollidone (Miscible)	20
Water	69
	100

Ink 4 was found to be unstable to storage because a precipitate formed after standing overnight. Therefore a freshly prepared sample of ink was used for the tests described in Table 1 below.

Example 3 - Ink Jet Printing Using the Inks

Inks 1, 2, 3 and 4 were printed onto Conqueror High White Wove plain paper 100g/m^2 from Arjo Wiggins Limited using a Hewlett Packard thermal ink-jet printer. The properties of the resultant prints are shown in Table 1 below.

The resultant prints had very good colour strength and brightness (chroma) as indicated in Table 1 and showed very high water fastness. 0.5ml of water run down a test print only 5 minutes after printing produced virtually no stain on the white paper.

Table 1

Ink	Ink stability	print quality	ROD	wet rub after 5 min
Ink 1	good	good	0.69	9
Ink 2	good	good	0.65	9
Ink 3 (Comparative)	poor	did not fire	x	x
Ink 4 (Comparative)	poor	good	0.907	10

ROD is the reflected optical density of the resultant print.

Wet rub after 5 minutes was scored 1 to 10 wherein 1 represents poor rub fastness and 10 represents excellent rub fastness.

Example 4

Further inks may be prepared having the formulations described in Tables 2 and 3 below wherein the following abbreviations are used. These inks may be applied to plain paper using an ink jet printer.

FRU : fructose
PU* : Identifies which of the polyurethanes as prepared in Examples 1 and 2 may be used. The number of parts by weight of PU is shown in brackets.
BZ : Benzyl alcohol
DEG : Diethylene glycol
DMB : Diethyleneglycol monobutyl ether
ACE : Acetone
IPA : Isopropyl alcohol
MEOH : Methanol
2P : 2-Pyrollidone
MIBK : Methylisobutyl ketone
SUR : Surfinol 465 (a surfactant)
PHO : K_2PO_4
TEN : triethanolamine
NMP : N-methylpyrollidone
TDG : Thiodiglycol
CAP : Caprolactam
BUT : Butylcellosolve
GLY : Glycerol
Colorant 1 : CuPc $(SO_2NHCH_2CH_2CH_2N(CH_2)_3)_{2.7}(SO_3H)_{0.3}$ wherein Pc is phthalocyanine.
Colorant 2 : The pyridone dye drawn on page 5 above.

TABLE 2

Colorant	Colorant Content	Water	Resin* (parts)	BZ	DEG	ACE	NaOH	$(NH_4)_2SO_4$	IPA	MEOH	2P	MIBK	BUT
1	2.0	58	1(10)	4	6						10	10	
2	3.0	61.8	1(10)	5	5		0.2				15		
1	2.1	60.9	2(6)	8							20	1	2
3	1.1	61.9	2(12)	9			0.5	0.5			9	5	1
1+2	(3+2)	54	3(5)	15	3	3			6		5	4	
1	5	50	2(15)	20					10				
2	2.4	51.6	1(5)	4		5				6	20	5	1
2	4.1	68.6	3(10)	5	2	10		0.3					
1	3.2	57.8	2(4)	5	4	6			5	4	6	5	
1	5	70	3(10)	6	2	2			1		4		
2	1.8	63.2	2(10)	5							15		5
1	3.3	63.7	2(12)	5		5				2		6	3
2	2.0	62.7	3(5)	10		7	0.3		3		10		
2	5.4	49.6	4(4)	20	2	1					15	3	
1	1.0	63	5(7)	5	4						15	5	

TABLE 3

Colorant	Colorant Content	Water	Resin (parts)	BZ	NMP	SUR	TEN	TDG	FRU	PHO	DMB	CH_3NH_2	CAP
2	1.5	63	1(10)	5		0.15	0.5	20					
1	2.5	60	2(15)	6	15					0.12			4
1	3.1	64	3(10)	8		0.3		15				0.2	
2	0.9	63	1(5)	10	20				0.5	0.2			
2	8.0	40	1(15)	15	15			5					2
2	4.0	67	2(10)	10	4				1		4	0.2	
1	2.2	67	2(10)	10	3				2		6		
2	9.0	54	3(15)	9	7		0.5			0.95	5		
2	5.0	57	2(10)	11				10			6		1
1	5.4	54	3(12)	5	17						7		
1	2.1	65	1(15)	5	5	0.1	0.2	2	0.5	0.1	5		
2	2	56	2(10)	10	5			12			5		
1	8	52	3(20)	5	8						5		2
1	10	63	2(13)	2							12		
1	10	71	1(5)	10			1	1				1	1

CLAIMS

1. An ink comprising water-dissipatable polyurethane, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent.

2. An ink according to claim 1 wherein the polyurethane has been obtained from the reaction of a mixture comprising the components:

   i) at least one organic polyisocyanate; and

   ii) at least one isocyanate-reactive compound providing dispersing groups.

3. An ink according to any one of the preceding claims wherein the colorant is soluble in the polyurethane.

4. An ink according to any one of the preceding claims wherein the water-immiscible organic solvent is benzyl alcohol.

5. An ink according to any one of the preceding claims comprising :

   (a) from 0.5 to 50 parts of a water-dissipatable polyurethane

   (b) from 0.1 to 20 parts of colorant;

   (c) from 40 to 90 parts of water;

   (d) from 2 to 30 parts of a water-immiscible organic solvent; and

   (e) from 2 to 60 parts of a water-miscible organic solvent;

   wherein all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) + (e) add up to 100.

6. An ink according to any one of the preceding claims wherein the polyurethane has a weight average molecular weight less than 25,000.

7. An ink according to any one of the preceding claims having a viscosity less than 20cp at 20°C.

8. An ink according to any one of the preceding claims for use in ink jet printer.

9. An ink according to any one of the preceding claims which is suitable for use in a thermal ink jet printer.

10. A process for printing an image on a substrate comprising applying thereto an ink according to any one of the preceding claims by means of an ink jet printer.

11. An ink jet printer cartridge containing an ink according to any one of claims 1 to 9